Peculiarities of the Helium-Beam Scattering on Metal Surfaces *

George Comsa, Gerda H. Comsa, and J. K. Fremerey

Institut für Physikalische Chemie der Universität Bonn

(Z. Naturforsch. **29 a**, 189—193 [1974]; received 19 October 1973)

Dedicated to Prof. Dr. W. Groth on the occasion of his 70th birthday

Some of the peculiarities of the atom scattering on metal surfaces are discussed in connection with the applicability of the Debye-Waller factor (DWF). The influence of the attractive potential well and of the finite size of the incident particles upon the scattering is commented. By comparing calculated DWF-values with experimental He scattering data it is concluded that the existence of diffraction is a necessary but not a sufficient condition for the applicability of the DWF. It is finally shown that the smooth potential surfaces which characterize the interaction between atoms and metal surfaces explain the apparently reduced thermal roughening observed experimentally.

Introduction

In the last few years the number of papers concerned with the scattering of molecular beams from solid surfaces increased dramatically. This justifies the appearance of two excellent reviews by Goodman[1] (theoretical) and Smith[2] (experimental). The rapid development can be ascribed on the one hand to the better technical means allowing for well defined experimental conditions (surface structure and cleanliness, well collimated beams, mass and velocity discrimination, etc.) and on the other hand to the search for informations of general interest. These informations concern not only the mechanisms and parameters of the gas-surface interaction (e.g interaction forces, surface catalysis) but also the solid surface itself (e.g. phonon spectra associated with the surface).

X-ray, electron and neutron beams were successfully used for a long time in the study of solids. It is thus obvious that the experience accumulated and the procedures developed during these studies should be used in the new field of investigation where atoms and molecules replace the former probing particles. But it is also evident that care should be exercised when making analogies, by bearing in mind not only the resemblances but also the differences.

One of the first procedures which was taken over in order to obtain informations about the surface Debye temperatures, T_{Ds}, by means of molecular beam scattering was the use of the Debye-Waller factor (DWF). Although attention was paid to the peculiarities of the gas-surface interaction (existence of an attractive potential well[3] and size effect[4]), the DWF was used not only to describe real diffraction peaks[4] but also specular peaks reflected from metal surfaces[5, 6] from which no diffraction was observed. We showed recently that the relative specular intensity measured in most He/metal surface scattering experiments is orders of magnitude larger than it should be expected from calculated DWF-values[7]. We explained the discrepancy by the fact that the specular peaks observed on most metals are not due to a diffraction process, and therefore concluded that the use of the DWF is at least questionable. Further, by analogy with the neutron scattering by crystals and on ground of Cassels'[8] systematization we showed[9] that, whereas the DWF accounts for the increase with temperature of the ordered inelastic scattering events at the expense of the ordered elastic ones, the events which produce the specular atom beams in the case of most metals belong to a third category: disordered elastic scattering. It was concluded that the existence of a diffraction process is a necessary condition for the correct application of the DWF.

It is the purpose of this paper to analyse the peculiarities of the atom scattering on metal surfaces and its consequences on the expression and value of the DWF. In the first section some aspects of the influence of the attractive potential well upon the scattering process are discussed. In the second section, values of the DWF calculated by considering a somewhat more elaborate size effect correction are presented. In both cases the comparison with experimental data shows that the He-beams specularly

Reprint requests to Dr. George Comsa, Institut für Physikalische Chemie der Universität Bonn, *D-5300 Bonn*, Wegelerstr. 12, Germany.

reflected from most metals cannot be described by the Debye-Waller theory probably because these beams are not zero-order diffraction beams. In the third section, the calculated DWF-values are compared with the experimental intensities obtained by Tendulkar and Stickney[10] in the sole experiment in which diffraction from clean metal surfaces was observed. It is finally concluded that the existence of simple diffraction is only a necessary but not a sufficient condition for the applicability of the DWF in atom beam/solid surface scattering.

I. The Attractive Potential Well

The first modification of the DWF-formula, allowing for one of the atom scattering peculiarities, was made by Beeby[3, 11]. He took into consideration the existence of the attractive potential well, $D = k T_{\text{min}}$, which characterizes all gas-solid interactions, and showed that "the momentum transfer appearing in the DWF is that calculated after the incident atom has been accelerated by the attractive part of the potential". In addition, he considered that the energy gained by the incident atom increases only the normal momentum. Thus, Beeby obtained the following expression for the DWF accounting for the diffraction of an incident atom at grazing incidence:

$$\delta_{\max} = e^{-2W} = \exp\left\{-\frac{24\, m\, T_s\, T_{\text{min}}}{M\, T_{\text{Ds}}^2}\right\} \quad (1)$$

where m and M are the masses of the incident and surface atom, respectively, and T_s is the surface temperature. The general expression of the DWF for an incidence angle Θ of the atom beam is[7] in the case of a monoenergetic beam of velocity v_g:

$$\delta_{v_g} = \delta_{\max} \exp\left\{-\frac{12\, m^2\, T_s\, v_g^2 \cos^2\Theta}{M\, k\, T_{\text{Ds}}^2}\right\}$$
$$= \exp\left\{-\frac{24\, m\, T_s}{M\, k\, T_{\text{Ds}}^2}\left(k\, T_{\text{min}} + \tfrac{1}{2}\, m\, v_g^2 \cos^2\Theta\right)\right\} \quad (2)$$

and in the case of a maxwellian beam of temperature T_g:

$$\delta_{T_g} = \delta_{\max}\left[1 + (T_g/T_{\text{min}})\, 2\, W \cos^2\Theta\right]^{-2}. \quad (2')$$

It is easy to see, that the "attraction potential correction", $\delta_{\max}$, is important even for He (smallest T_{min}), its influence growing with the decrease of the beam temperature and with the increase of the angle of incidence.

It is apparent from (2) and (2′) that the diffracted beam intensities should decrease with increasing beam temperature. Indeed, Estermann and Stern[12] observed (on a non-metallic surface, LiF) a decrease of the specularly reflected intensity with increasing He-beam temperature. However, Stoll et al.[13] found in the case of Pt(111) that "increasing the He-beam temperature increases the value of the peak maximum and decreases the width of the scattering pattern". This is, besides the quantitative considerations we presented elsewhere[7] and which we will discuss in the next section, a very strong argument for the non-diffractive character of the He-beams specularly reflected from metal surfaces, and thus for the non-applicability of the DWF.

In order to comment on this argument, we will give a short review of the systematization of the atom/surface scattering processes we recently proposed[9]. This systematization was obtained by analogy with the neutron/crystal scattering theory due to Cassels[8]. The scattering processes are divided into four categories:

1) Ordered elastic: real diffraction peaks (e. g. He/LiF).
2) Ordered inelastic: diffraction processes including phonon interactions, e. g. the streaks found by Williams[14] in the vicinity of the He-peaks diffraction from a LiF(001) surface.
3) Disordered elastic: e. g. the central portion of the specularly reflected He-peaks (from metals).
4) Disordered inelastic: trapping-like mechanisms, e. g. the diffusely scattered atoms and probably also the wings of the He-beams specularly reflected from some metals.

To the first two categories belong those scattering processes which are characterized by the coherent interference of the waves scattered from discrete sites (i. e. from the individual surface oscillators). In the third category we have included the He-atoms specularly reflected from metal surfaces on which no diffraction was observed (no coherence). This is actually in accordance with the common view that, in the case of metals, the He-atoms are scattered by a smooth surface and not by discrete sites. Each point of this smooth potential surface is built up by the superposition of the long range interaction potentials (incident-atom/surface-atom) belonging to several surface atoms. This means that the He-atom actually collides with a large mass, the collision being practically elastic. Finally, the forth category contains the scattering processes during which a trapping-like event occurs which is obviously incoherent and inelastic.

In the slow neutron and low energy electron scattering the first two categories are usually called Bragg scattering and "one phonon + multiphonon" scattering, respectively. It was theoretically shown and experimentally confirmed [15] that the sum of the scattered electrons belonging to these two categories is constant over a wide surface temperature range. There is no reason to assume a priori that this is true also for the atom scattering. On the contrary: Weinberg and Merrill [16] showed on the basis of an "attractive square well and impulsive repulsive potential model" that the trapping probability decreases with increasing surface temperature and also with increasing beam temperature. This means that if the scattering on a given surface consists of processes of type (1), (2) and (4) [17], the sum of the ordered scattering events (1) and (2) will increase with increasing surface temperature (and/or beam temperature) at the expense of the type (4) events. On the other hand, the transfer between the two "ordered" categories is governed by the DWF: by increasing the surface temperature (and the beam temperature as well) the number of inelastic events (2) increases at the expense of the elastic ones (1). One may thus conclude that, by increasing the surface temperature and/or the beam temperature the number of ordered inelastic events (phonon interactions) always increases due to both the relative decrease of the number of ordered elastic events (DWF) and the absolute decrease of the trapping. A similar statement concerning the variation of the ordered elastic events can hardly be made, because the number of these events increases on account of the decrease of trapping but decreases on account of the DWF.

One may draw a practical conclusion from the above considerations: in order to obtain quantitative informations by means of the DWF, its value (or its variation) has to be compared with the ratio (1)/[(1) + (2)] and not with (1)/[(1) + (2) + (3) + (4)]. Unfortunately, it is not easy to distinguish experimentally between (1) + (2) and the sum of all events.

Returning now to the results obtained by Stoll et al. [13] for the system He/Pt(111), it seems natural to consider the central portion of the specular peak as consisting of disordered but elastically scattered atoms [type (3)] and to assume the atoms contributing to the wings of the peak as having undergone a trapping like process [type (4)]. As was shown by Weinberg and Merrill [16], the trapping is reduced by increasing the beam temperature, and thus the above cited observation of Stoll et al. can be easily explained [18].

II. The Size Effect Correction

Recently, Hoinkes et al. [4] have suggested a correction of the DWF for the case of atom scattering which accounts for the finite size of the scattered particles (comparable to the size of the scatterers). While an electron always probes only one surface atom, an incident atom may probe simultaneously 1, 2, 3 or 4 surface atoms. As the incident atom collides only with the furthest out of them, the mean square displacement of the surface atoms is apparently reduced. Hoinkes et al., assuming independent surface oscillators, have calculated this reduction for the H_1/LiF system and obtained a significant increase of the DWF. Although it seems questionable to introduce this correction, which is based on a very classical argument, in a typical quantum-mechanical formula, we applied it to the systems He/Ag(111), Pt(111) and W(110). By following consequently Hoinkes' argument we concluded that, as an incident atom collides always with the furthest out of the surface atoms which it is probing, also the mean collision surface is apparently displaced. Thus we calculated the mean square displacement of the surface oscillators relative to the apparently displaced surface. These results, which we checked by electronic simulation, led us to the δ_s-values of the DWF, which account for the size effect correction. In order to compare calculated DWF-values with experimental relative intensities, one may use the expression of the scattered intensity given by Weinberg [6]:

$$I_r = |F_{hkl}|^2 \, \delta_s \qquad (3)$$

where $|F_{hkl}|^2$ is the intensity scattered by the rigid lattice. As it is obvious that $|F_{hkl}|^2$ is smaller than the incident intensity, I_i, one always should have:

$$I_r/I_i < \delta_s \, . \qquad (3')$$

One can see from Table 1 that for Ag(111) and Pt(111) even the δ_s-values, although being significantly larger than the uncorrected δT_g-values, are orders of magnitude smaller than the experimental relative intensities[21]. This is in flagrant contradiction to relation (3′) and therefore leads to the same conclusion as the qualitative argument in the preceding section and the dicussion of the uncorrected DWF-values: the DWF cannot be applied to the He-atom beams specularly reflected from metal surfaces, probably because this specular reflection is not a zero-order diffraction but a kind of total reflection on a smooth potential surface (by analogy with the total reflection of glancing slow neutron beams).

The rather good coincidence between experiment and the δ_s-values in the case of *W*(110) is probably accidental. This will become evident in the next section.

III. The He-Diffraction Peaks from Clean *W*(112) Surfaces

The DWF-values calculated by considering the parameters of the Tendulkar and Stickney[10] experiment are even smaller than those given in Table 1 for (Ag(111) and Pt(111)[7]. Indeed, they are ranging from 10^{-3} to 10^{-8}. This is mainly due to the very high surface temperatures (1300 °K and 2200 °K) used in the experiment. The discrepancy is so important that the size effect correction cannot improve the situation significantly. (In addition, the correction is less important in the case of a (112) surface.)

Table 1. Specular He-intensities vs. valculated δT_g and δ_s [a].

Surface	T_s (°K)	T_g (°K)	θ	I_r/I_i		δT_g	δ_s
Ag(111)	296	296	20°	.21	Ref. [19]	.013	.050
	296	296	45°	.37		.028	.096
	296	296	65°	.32 [d]		.077	.205
$T_{min}=150$ °K [b]	373	296	45°	.29		.014	.058
$T_{Ds}=155$ °K [c]	573	296	45°	.14		$.002_4$	.018
Pt(111)	373	296	45°	.20	Ref. [13]	$.009_7$	.048
	373	973	45°	.25		$.001_5$	$.007_1$
$T_{min}=150$ °K [b]	573	296	45°	.15		$.001_5$	.013
	573	973	45°	.17		$.000_2$	$.001_5$
$T_{Ds}=110$ °K [c]	773	296	45°	.10		$.000_3$	$.004_3$
	773	973	45°	.13		$.000_{03}$	$.000_4$
W(110)	375	296	45°	.16	Ref. [20]	.113	.226
$T_{min}=150$ °K [b]	575	296	45°	.14		.044	.114
$T_{Ds}=180$ °K [c]	775	296	45°	.12		.019	.061

[a] δ_s includes the "size effect correction".

[b] After Reference 3.

[c] After Reference 11.

[d] The value for 65° is actually higher because a portion of the incident beam misses the target surface at grazing angles.

We are actually in a rather confusing situation: Tendulkar and Stickney have observed not only specular beams but also higher order diffraction peaks located at the expected positions and, in spite of this, all these peaks are orders of magnitude higher than the calculated DWF, which is in flagrant contradiction with formula (3′). There is no reason to suspect the diffractional character of the peaks observed or the cleanliness of the tungsten surface. A possible explanation of the non-applicability of the DWF even to diffraction peaks of He-atoms scattered from metal surfaces might be the following. The interaction potential surfaces between the incident He-atom and the W(112) surface are smooth, as in the case of other metal surfaces (i. e. no projections due to individual atoms). But, on account of the very prominent surface atom rows which characterize the W(112) surface, the smooth potential surface becomes wavy, i. e. a kind of linear grating. The incident He-atom beams directed normally to the grating lines ($\Theta = 0°$) may undergo diffraction. However this diffraction process does not correspond to the definition of the DWF which involves a diffraction process consisting of the coherent interference of waves scattered from individual surface oscillators. The diffraction which takes place on the W(112) surface is produced by the coherent interference of the waves scattered from a wavy smooth potential surface, i. e. again from a potential built up by the superposition of individual potentials. A simple proof of this affirmation is the fact that by changing the azimuth angle of the plane of incidence ($\Theta = 90°$, i. e. parallel to the waves) Tendulkar and Stickney noticed the complete disappearance of diffraction.

One is led to the conclusion that the mere existence of diffraction is not a sufficient condition for the use of the DWF in the atom beam scattering from surfaces. There is an additional condition which has to be fulfilled: it should be proved for each separate case that the diffraction is produced by the coherent interference of the atomic waves scattered from individual surface oscillators.

Two additional remarks:

1) The fact that for metals the experimental relative intensities turn out to be orders of magnitude larger than the DWF is equivalent to the exis-

tence of apparent surface temperatures much lower than the real ones. This apparently reduced thermal roughness of the surface is in accordance with the circumstance that for metals the scattering takes place on a smooth potential surface built up by the superposition of several long range individual potentials. The thermal roughening of this outer potential surface reflects only weakly the thermal displacements of the individual oscillators[22].

2) The existence of atom diffraction peaks (i. e. elastic and coherent) which are not produced by the coherent interference of the waves scattered from individual oscillators sets already a first limit to the analogy with the neutron scattering. This is due to the fact that the interaction potential between neutrons and crystal atoms is of very short range, the neutron "seeing" a smooth surface (total reflection) only for glancing angles below one degree. We are thus forced to introduce in the classification presented in the first section a new category, say (1′), comprising the ordered elastic scattering events which take place on potential surfaces built up by the superposition of the potentials of several individual oscillators.

Conclusion

The analysis of some peculiarities of the atom scattering on metal surfaces in connection with the DWF leads to the conclusion that the existence of diffraction peaks is a necessary[7, 9] but not a sufficient condition for the applicability of the DWF. It should be proved for each separate case that the diffraction is produced by the coherent interference of atomic waves scattered from individual surface oscillators. The sole diffraction pattern yet observed on clean metal surfaces[10] seems to be produced by the coherent scattering on a wavy but smooth interaction potential surface. Since each point of this surface is built up by the superposition of several interaction potentials, the thermal roughness of the metal surfaces is apparently strongly reduced.

According to our above considerations the effective thermal roughness of the outer potential surface is related to the actual motion of the individual oscillators. The temperature dependence of the relative intensities of specularly reflected atom beams might be used for the determination of surface Debye temperatures, provided that the proper relationship between the effective thermal roughness and the oscillation of the surface atoms can be found.

Acknowledgements

The authors are much indebted to Professor Dr. H. D. Beckey and Professor Dr. W. Groth for their continuous support.

---

[*] Work supported by Deutsche Forschungsgemeinschaft.

[1] F. O. Goodman, Surface Sci. **26**, 327 [1971].

[2] J. N. Smith Jr., Surface Sci. **34**, 613 [1973].

[3] J. L. Beeby, J. Phys. C, Solid St. Phys. **4**, L 359 [1971].

[4] H. Hoinkes, H. Nahr, and H. Wilsch, Surface Sci. **33**, 516 [1972].

[5] B. F. Mason and B. R. Williams, J. Chem. Phys. **57**, 872 [1972].

[6] W. H. Weinberg, J. Chem. Phys. **57**, 5463 [1972].

[7] G. Comsa, J. Phys. C, Solid St. Phys. **6**, 2648 [1973].

[8] J. M. Cassels, Progress in Nuclear Physics: I, ed. O. R. Frisch, Butterworth-Springer, London 1950, p. 185.

[9] G. Comsa, G. H. Comsa, and J. K. Fremerey, Proc. Int. Conf. Surf. Phen. Madrid 1973 (in press).

[10] D. V. Tendulkar and R. E. Stickney, Surface Sci. **27**, 516 [1971].

[11] see also W. H. Weinberg, J. Phys. C, Solid St. Phys. **5**, 2098 [1972].

[12] I. Estermann and O. Stern, Z. Phys. **61**, 95 [1930].

[13] A. G. Stoll, D. L. Smith, and R. P. Merrill, J. Chem. Phys. **54**, 163 [1971].

[14] B. R. Williams, J. Chem. Phys. **55**, 3220 [1971].

[15] R. F. Barnes, M. G. Lagally, and M. B. Webb, Phys. Rev. **171**, 627 [1968].

[16] W. H. Weinberg and R. P. Merrill, J. Vac. Sci. Technol. **8**, 718 [1971].

[17] Scattering of type (1) and (2) can hardly coexist with type (3) because the former two imply discrete scattering sites and the latter a smooth potential surface.

[18] There is however a weak point in this explanation: Weinberg and Merrill[16] consider the trapping probability of the He-atoms at the experiment temperatures as being negligible. This is the reason why we used the expression "trapping-like process" and maintained the discussion at a qualitative level. The more general term "inelastic process" is inadequate for this case because it includes also the phonon interaction, the beam temperature dependence of which is exactly opposite to that of the trapping.

[19] R. Sau and R. P. Merrill, Surface Sci. **34**, 268 [1973].

[20] W. H. Weinberg and R. P. Merrill, J. Chem. Phys. **56**, 2881 [1972].

[21] The reflected intensities are not reported to the sum (1) + (2), as recommended above (I_i represents all scattering events). If this had been done the dicrepancy would have been even larger.

[22] It is noteworthy that the concept of the incident atom colliding with the smooth potential surface has some similarities with the idea (of Hoinkes et al.[4]) concerning the incident atoms probing 1, 2, 3 or 4 surface atoms. A main difference consists in the fact that while in the former case the incident atom collides with a superposition of potentials (i. e. simultaneously with several atoms), in the latter it collides only with the furthest out of them. However, both concepts lead to an apparent reduction of the surface thermal roughness. We think that the idea of Hoinkes et al. may be successfully applied to systems like H_1 , He/LiF, while the smooth potential concept seems suitable to He/metal systems.